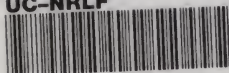


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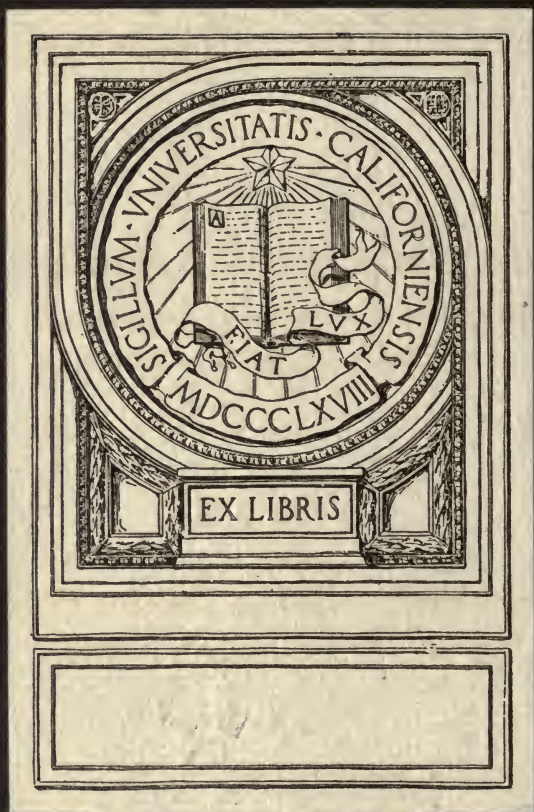
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PHYSICAL CHEMISTRY
AND
SCIENTIFIC THOUGHT

An Inaugural Lecture

*delivered at the University of Liverpool
on Friday, 16 January, 1914*

BY

W. C. McC. LEWIS, M.A., D.Sc.

BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY

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PHYSICAL CHEMISTRY AND SCIENTIFIC THOUGHT

LADIES AND GENTLEMEN.—At the outset I should like to say that the subject-matter of my remarks this afternoon can scarcely be regarded as novel. There are, however, one or two points which, although not new, are sufficiently important in themselves to merit emphasis, especially if, as I presume is the case, there are some here who may have recently decided to devote themselves to some branch of science as their life's work.

The considerations which I wish to bring before you may be dealt with in the following order. In the first place I should like to say a little about philosophic ideas and principles in general, and then to pass on to that department of philosophy which we distinguish as natural philosophy or science, considering as a special case the two closely allied sciences of chemistry and physics which together have given rise in relatively recent years to the science of physical chemistry. Lastly I shall say a word regarding the significance of research, especially in connection with some of the problems of physical chemistry.

I should like, first of all, to draw your attention to that process of the mind which we call *thought*. Thinking may be defined as 'the activity of the mind which discovers the order, arrangement and system in the reality that the senses reveal. Without thought our felt experience would be a chaos, and not a world.' *Serious* thought is, to my mind, to be distinguished from the untrained and unco-ordinated exercise of thinking by the quality it possesses in respect of direction. Serious thought is directed

thought. It does not consist of a series of isolated or discontinuous processes, but is caused to grow and develop along definite lines, partly indeed by haphazard observation, but mainly by what we call education or mental training in its best sense. It is clear that serious thought, if it is to be serious at all, must have an objective. The more immediate aims of different lines of directed mental effort may be totally dissimilar, but ultimately they must all lead to the same goal, namely, the discovery and apprehension of *truth*. Truth, it has been well said, 'is in effect the ideal of logical consistency.' The attainment of truth is the attainment of the knowledge of reality. I might mention in passing that in connection with such attainment even to a small measure, and in cases which from the general standpoint of mankind might be regarded as relatively unimportant—for example, the results of some particular piece of specialised research—it is a perfectly general and at the same time remarkable experience that such attainment carries with it varying degrees of mental satisfaction, in proportion in fact as our thinking approximates to reality. I shall not attempt to go into the connection between realisation of truth and the mental satisfaction it produces; it is sufficient to point out that for practical purposes they may be regarded as identical. We may, therefore, say that the objective of serious thought is, in a sense, the mental satisfaction which results from it. The man who feels any restlessness of mind, who is conscious of being continually spurred on to enquire into the why and the wherefore of things—and every rational being feels this at least to some extent—the man who feels such a desire and honestly strives to satisfy it, even to a small degree, may make a humble, but at the same time a just and proper claim to the honoured title of

philosopher. For, after all, philosophy is actually the love of wisdom, and its goal the nature of reality.

+ As I have just said, Philosophy has its root and origin in the desire of mankind to try and understand things. Now, it is by no means easy to give an adequate definition of what we mean when we say that we understand or do not understand a given statement of observation or deduction. What, in short, do we mean when we use the term *explanation* in the scientific sense? Let me by way of parenthesis quote some words from a recent writer in regard to our relation to the problem of reality. 'There are two attitudes,' he says, 'to the problem of truth and reality—that of the mind which brings a practical test to every question, and that of the mind restless to gain by insight or by speculation a clue to the mystery that enshrouds the meaning of existence. The first attitude seems peculiarly to characterise the man of science, who delights to think that the problem of reality is simple and open to the meanest understanding. Between the plain man's view and that of the man of high attainment in scientific research there is for him only a difference of degree, and science seems almost to require an apology if it does not directly enlarge our command over nature. It would explain life and consciousness as the result of chemical combination of material elements. Philosophy, on the other hand, is the instinctive feeling that the secret of the universe is not open and revealed to the plain man guided by commonsense experience alone, even if to this experience be added the highest attainments of scientific research. Either there is far more in matter than is contained in the three dimensional space it occupies, or else the universe must owe its development to something beyond matter. The

universe, indeed, must seem a poor thing to a man who can think that physical science does or can lay bare its meaning. It is the intense desire to catch some glimpse of its meaning that leads the philosopher to strive to transcend the actual world by following the speculative bent of the reasoning power that his intellectual nature makes possible.'

I quote these words as illustrating how the human mind endeavours to analyse its relation towards reality in general terms. I totally dissent, however, from the antithetical juxtaposition in which the terms philosophy and science are employed, for, to my mind, any man who has followed a line of directed thought is necessarily a philosopher, and science is really only a particular form of philosophy. It is related of the great Faraday that he delighted to be referred to as a natural philosopher above any other title. The true scientist no longer attempts to explain life and consciousness 'simply as the result of chemical combination.' We have passed, I hope, from the dogmatic and narrow materialism which characterised science some thirty or forty years ago. In our own lifetime we have seen scientific conclusions which were once regarded as permanently unassailable prove incapable of comprehending the results of more recent observation and deduction, such, for example, as the doctrine of the immutability of the elements. It is a commonplace nowadays to say that knowledge is not absolute, but relative—that, in fact, it goes on growing even in fundamental conceptions, and the beliefs of the present age will be modified or discarded altogether by the succeeding.

I do not wish, however, to deal at greater length with the problems of philosophy in general, but to pass on to the more immediate aims of science. The primary object of any science is *generalisation*.

According to the types of problems and phenomena met with, and consequently according to the nature of the generalisations which embrace these, it has been found convenient to split up science into a number of sub-divisions more or less closely allied. Such divisions are, indeed, arbitrary, the result of practical expediency, having their origin in the almost boundless extent of science as a whole, and the consequent inability of any one mind to satisfactorily explore even to a limited extent the whole range of natural phenomena. We shall therefore restrict ourselves in what follows to two regions which lie very closely together, namely, physics and chemistry, and spend a little time in considering some of the general principles which are common to both.

Let us return at this point to the question which we have already asked ourselves, namely, what do we mean when we say that we have explained some phenomenon—in the present case some chemical or physical phenomenon?

Explanation is a term which is frequently upon our lips; in fact, we meet with no new phenomenon in physics or chemistry without instantly striving to account for it. Such explanation, when we analyse it, consists ultimately in the restatement of the phenomenon in terms of mechanics. By restatement I do not mean the mere use of alternative terms, but rather the demonstration that the existence of the phenomenon is to be anticipated on the basis of a series of logical mechanical theorems (which we have reason for regarding as true) often with the addition of something which we find necessary as a connecting link, and to which we give the name of assumption or hypothesis; that is something which we had not previously realised as true, and which, therefore, calls for experimental

verification, direct if possible, or at any rate indirect, through the medium of some deduction which is based clearly and unequivocally upon it. The discovery of a new phenomenon or relationship and its elucidation by means of a cautious employment of hypothesis verified directly or indirectly by the most rigorous means which suggest themselves, should be the characteristic of every properly conducted research. Sometimes, of course, the necessary connecting link, the hypothesis, is apparently not verifiable in the ordinary sense, except that it is not known to stand at variance with any reliable experimental fact or deduction. This in itself is not sufficient evidence that the assumption is true—it only *may* be true. Let us take a familiar illustration. The basis of the molecular or kinetic theory of matter—that is, the real existence of molecules—was regarded for a long time with a certain amount of suspicion, even by those who were ready enough to admit and appreciate the usefulness of the kinetic hypothesis, and the reason for this was simply that indicated above. Of course, the fact that the kinetic theory was able to afford a very simple and reasonable explanation of the behaviour of gases in regard to volume, pressure, and temperature relations was strong indirect evidence of its validity, though this was partly counterbalanced by the fact that the behaviour of gases when much compressed, and still more the behaviour of liquids and solids, could not be accounted for without the introduction of some further assumptions such as the existence of forces of attraction between the molecules. The final vindication of the kinetic theory in respect of the experimental demonstration that molecules *do* exist has indeed only been completed within the last decade by the noted French physicist, Jean Perrin, and independently by Millikan in America and

Svedberg in Sweden. It is clear that the problem of experimental verification of an hypothesis is one of primary importance. The chemist or physicist should not only possess the imaginative faculty which will bring a new concept into being, he should equally possess the critical faculty which will enable him to choose aright between a number of possible hypotheses. Science owes little to the man of untutored imagination, be it ever so fertile. It owes more—but not much more—to the mind which can destroy a faulty structure, but can build nothing from the ruins. The proper relation of theory to experiment is one which must always bring itself very forcibly to the notice of the investigator. Chemical or physical theory represents the accumulation of logical mechanical notions linked together by means of verified or partially verified hypotheses. It is the fact of verification which distinguishes a theory from an hypothesis.

The lines of thought involved in theoretical scientific speculation possess at least one characteristic which at first sight is not a little surprising. That theory which is *simplest* is generally and rightly regarded as truest, provided, of course, it is wide enough to embrace all the known facts; yet this very simplification is most frequently introduced into our reasoning through the medium of attributes which can be conceived of, but cannot be realised in actual practice. We speak, for example, of the perfect gas, weightless strings, frictionless pistons, a perfect vacuum, absolute zero of temperature, and so on. Such things cannot be realised by experiment, and yet it is only by their introduction that we have been able in general to work out consistent relations applicable to actual phenomena. We are so accustomed to make use of these simplifications—and we are, of course, absolutely justified in using

them—that we are apt to lose sight of the fact that we are making such assumptions at all. It is important, therefore, to bear in mind that with respect to theoretical conclusions every experimental verification is necessarily approximate in this sense. In addition to this, as every experimenter knows, it is impossible to completely eliminate experimental error, due both to the apparatus itself and the personal equation of the experimenter. We always try, of course, to so arrange matters that the error shall be the least possible, and a good experimenter is simply one who partly by intuition, partly by natural skill supplemented by experience, is able to select those conditions in which this unavoidable error is reduced to a minimum. As already stated, the verification of a theoretical conclusion cannot be absolute, though in the most favourable cases it may become practically so. It is a characteristic of the truly scientific mind that it is capable of distinguishing, at least in many cases, a real approximate verification, that is a satisfactory verification—and, remember, there are varying degrees of approximation—from false or apparent verification, be it ever so close. The distinction is not infrequently a subtle and, therefore, a difficult one. One has often to weigh many apparently trifling considerations, chance observations, unexpected side effects. One can learn much by experience, but at the same time the experimentalist of the first rank is to a very large measure born, not made.

I have said that our so-called ‘explanations’ of chemical and physical phenomena consist in the application of mechanical concepts. It is obvious, therefore, that such explanations are after all partial; but it is not improbable that this is as far as our mental limitations will permit us to go. Although, for example, in that system of logic to which we

give the name 'Thermodynamics' an attempt, and a successful one, too, is made to get beyond what might be called the more crude mechanical notions involved in the application of the kinetic theory to the problems of the constitution and behaviour of matter, the fact that thermodynamical reasoning simply in virtue of its abstractness has presented great—sometimes very great—barriers to the average intelligence as regards the comprehension of truths even when these have already been put into explicit terms by greater minds—the fact that this difficulty exists is very clear evidence, I think, that our minds are naturally more fitted to adjust themselves to mechanical concepts. The chemical and physical advances of the future will be made by the simultaneous application of concrete mechanical notions and the more abstract conclusions of energetics. Indeed, the remarkable advance which has recently been made in our knowledge regarding the *solid* state of matter, through the introduction of the unitary theory of energy as applied to resonators of atomic size, in the hands of Planck, Einstein, Nernst, and their collaborators, is the most striking instance of the great results which may be obtained by the union of thermodynamics and kinetics. Not only, for example, do we possess a reasonable explanation of the Law of Dulong and Petit regarding the constancy of the heat capacity of atoms in solids, but, still more, we possess an equally reasonable explanation of the numerous deviations from the law which have been long known to exist. Planck's conception, too, of the meaning of Nernst's 'Heat Theorem,' which for the first time demonstrated how the affinity of a given chemical reaction could be correctly calculated from the heat of the reaction, is another case in point.

In making the rather disappointing statement, a

few moments ago, regarding the fact that our explanation of phenomena could only be considered as partial, it might be supposed that we were taking from science just those elements which make scientific investigation worth while. To a certain extent this is true. At the same time a little closer inspection, some familiarity with the 'mechanism' of our theoretical and experimental operations, will not fail to reveal the fact that all that we are really capable of extracting from science, not only as regards the mental satisfaction of the pure scientist in the interpretation of phenomena, but also as regards the more utilitarian aims of the worker on the applied side, stands undiminished. The knowable is vast compared with the known. In that, indeed, we find the *raison d'être* of all research.

I should like to pass on from this very cursory review of general principles to the problem of their significance from the standpoint of research itself. For research of any kind consists ultimately of these principles in active operation and application.

Research in chemistry and physics may, broadly speaking, be divided into three classes: First, researches in which theoretical considerations and speculations play the entire or at any rate the most important *rôle*, such as we find, for example, in investigations in mathematical physics and theories of electricity, optics, heat and capillarity; secondly, researches in which an idea inspired by previous theoretical or experimental results is developed in such a way as to be put more or less conveniently to experimental test. The whole field of physical chemistry may be cited as an illustration of this class. Thirdly, there are researches in which the aim and object is essentially experimental, the interest lying not so much in the theoretical significance of the results themselves as in their usefulness

from the standpoint of accumulation of sound experimental data, such as one finds for example in determinations of atomic weights and stoichiometric work in general. All these are essential to scientific progress, though I imagine the second is likely to prove the most generally attractive. For the third class, indeed, relatively few are either fitted or willing, as success depends so largely upon innate skill and unwearying patience in view of the somewhat unexciting nature of the work. One must not dogmatise, of course, as to how any investigation is going to turn out—it was, after all, the observation of a slight anomaly in the density of a gas observed by Lord Rayleigh which led in the hands of Ramsay to the discovery of argon and the other members of the rare gas group. Naturally, such divisions as I have mentioned are in actual practice by no means sharply defined. Research in physical chemistry, indeed, progresses along all three, though almost entirely through the medium of the second.

In connection with the scope of physico-chemical research, I think that at this point a legitimate digression might be made, if I draw your attention to a perfectly natural and at the same time quite general scheme or system which serves to link together the many scattered areas which go to form the wide domain of physical chemistry. The term scheme or system has perhaps something of a reputation—a rather unsavoury reputation—in the opinion of a good many people who are apt to associate with it a certain cramping or fettering of action—an extremely undesirable effect to produce on any scientific imagination. In my opinion, however, it is a matter of some importance that a worker engaged say in some specialised branch of physico-chemical investigation should possess at least a generally correct idea of the ultimate relation

which his own work bears to that of his neighbour, however dissimilar the immediate object of each investigation may be. As a starting point, let us think of matter associated with energy. From this we may pass to the concept of equilibrium, since all material systems tend towards this state, which is conditioned by a certain distribution of both matter and energy. For simplicity's sake let us fix our attention upon that kind of equilibrium which is known as dynamic. In this case the state of equilibrium, which is necessarily characterised as far as the material system is concerned by absence of change throughout infinite time, the equilibrium arises from the mutually annulling effect or balance of equal and oppositely directed sets of forces, which are associated with the molecules, atoms, ions or electrons which compose the material system in question. We are not necessarily restricting ourselves to the contemplation of such equilibria from the kinetic standpoint alone; we are also at liberty to take into consideration the energy changes involved. That is to say, we can regard the behaviour of matter both from the kinetic and thermodynamic standpoints. Now it is clear that every conceivable material system is necessarily either already in equilibrium or has not yet reached equilibrium. This general division, according to the existence or non-existence of equilibrium, is the basis of the scheme or system of classification which I wish to bring before you here. It is obvious that it possesses the the double advantage of offering a natural mode of classification of phenomena already known, and at the same time is capable of including within its scope phenomena which the future has still to disclose. In this connection let us consider for a few minutes some of the types of physico-chemical equilibria with which we are acquainted. We naturally turn in the first

instance to the simplest kind, namely, that which might be called the purely physical, which deals with the problem of the distribution of molecules in space. With this type of equilibrium we associate the so-called 'perfect gas' laws of Boyle, Gay-Lussac, and Joule, the equations of state for imperfect gases, vapours, and liquids, the principle of the continuity of the gaseous and liquid states, and, finally, the new theory of Planck and Einstein regarding the behaviour of the solid state. Turning now to types of equilibria which we may call in a stricter sense 'chemical,' we may at the outset divide these up for convenience sake into equilibria in homogeneous or one-phase systems and equilibria in heterogeneous or polyphase systems. Chemical equilibria in homogeneous systems may be further sub-divided according to the physical state of the system, i.e., whether it be gaseous, liquid or solid. If gaseous, the equilibria which manifest themselves are dealt with by means of the principle known as the 'law of mass-action,' which leads us to the concept of an equilibrium constant and the conditions under which we may expect a variation of such a constant by alteration in parameters such as temperature and pressure. Much work still remains to be done in the accurate determination of gaseous equilibria constants, mainly in connection with the affinities of the reacting molecules and atoms. But, in addition to homogeneous gaseous equilibria, we have likewise similar types of equilibria in liquid systems both in mixtures of liquids and in solutions to which the same law of mass action once more applies. To this group also belong those relations which exist between the reactivity of electrically charged atoms or ions and uncharged molecules which are taken account of in the theory of electrolytic dissociation, with its manifold applications not

only in inorganic and organic chemistry, but in biochemistry as well. Lastly we have equilibria in homogeneous solid systems—a field of great difficulty for the investigator, and, therefore, still practically unworked, but, nevertheless, offering great attraction, especially to those who have at their disposal the means of investigation at high temperatures.

Passing on now to the consideration of equilibria in heterogeneous systems, we find ourselves looking out over an even greater expanse ready and waiting for investigation by the application of those principles which we have just considered, and in addition by the application of that marvellous generalisation which originated in the mind of the famous American mathematician Willard Gibbs, and which first became a really effective means of research in the hands of the Dutch chemist, Bakhuis Roozeboom—I mean the Phase Law. In addition to these varied types of thermal equilibria we must not overlook those other equilibria to which we give the name of photochemical equilibria, or, more correctly speaking, ‘stationary states,’ which form one of the most important developments in the domain of photochemistry.

So much for systems actually in equilibrium. Let us turn now to systems which are in a state of transition or change tending, either slowly or rapidly, towards equilibrium. To this division belongs the study of the whole range of chemical kinetics in homogeneous and heterogeneous systems, the determination of ordinary or thermal reaction velocities in terms of the law of mass action, the alteration of velocity with temperature and pressure, the phenomenon of catalysis, and in addition those reactions which are brought about under the influence of radiant energy—the so-called photochemical re-

actions. We have likewise to take into account the problems of affinity—not in its old and vague sense, but in terms of the newer ideas of van 't Hoff, in which affinity is measured quantitatively by maximum work—and the absolutely fundamental connection which, within the last decade, has been shown, by the noted German physical chemist, Walther Nernst, to exist between the heat of a reaction and the true affinity of the process. Of all the fields of investigation which I have mentioned none to my mind offer such attraction at the present time, or are more likely to repay investigation as those of photochemistry and chemical affinity.

All that I have said about physico-chemical research refers in the first instance to the purely scientific side of the subject. I have not attempted to deal with the applied side. One important department of work of this kind should be mentioned, simply on account of the relatively small progress which has up to the present been made—I refer to electrothermics and heavy electro-chemistry generally, which subjects are forming to an ever-increasing extent the basis of modern chemical industry.

To return to the question of research in general, from the more or less philosophic standpoint; I should like to have touched upon the question of success in research work, and the conditions which may be reasonably considered as making for its attainment, but the subject becomes too speculative, and time only permits of a passing reference. Let me quote the words of Faraday—words of warning, though not altogether of discouragement: ‘ . . . the world little knows how many of the thoughts and theories that have passed through the mind of a scientific investigator have been crushed in silence and secrecy by his own severe criticism and adverse

examination—that in the most successful instances not a tenth of the suggestions, the hopes, the wishes, the preliminary conclusions, have been realised.’ Remember that these are the words of one of the most brilliant investigators and one of the most profound thinkers whom science has ever known.

Perhaps at this juncture it may not be out of place to deal quite briefly with a very practical point, namely, the method of initiation of an individual into his first original investigation. The responsibility of the suggestion of a subject will rest with the person under whose guidance the work is being carried out. This guidance, as a matter of fact, is a very variable quantity, and is usually determined to a certain extent by the nature of the research itself, by the kind of response which the student makes, his fertility in contrivance in overcoming experimental difficulty, his accuracy and reliability, his alertness in observing fortuitous and unexpected phenomena, and, above all, his appreciation of the significance of his own work in so far as it suggests still further investigation and extension. Some people lay great stress upon an exhaustive examination of the literature as an essential preliminary. Undoubtedly some acquaintance with previous work must be obtained at the outset, but I am inclined to think that the comprehensive survey of earlier investigation, which, of course, must be made in all cases, is best carried out concurrently with the earlier preliminary experiments themselves. This has the advantage of preventing the beginner attacking a subject in a manner which has perhaps become stereotyped, and from which mode of attack possibly little more is to be gained, and at the same time it prevents the repetition of already ascertained facts unless indeed the existence of the facts themselves are in doubt. It is a most deplor-

able state of things to see, in reading over any summary of current research, the amount of work which is done evidently with little more aim or object than to add one more illustration of a well-established principle, without any indication that the principle itself has thereby been widened or modified in its application. Such work is a travesty on the name of research. I am not, for one moment, claiming that the object one actually starts out with must be rigidly adhered to in every case. In some cases it happens that, despite every care we may take in the selection of a subject as a good one and a reasonably feasible one, we find that the investigation takes quite an unexpected turn. It is not necessarily any the worse research on that account—in fact, it may turn out very much the better, and as I have already said, one of the best qualities of any investigator is the possession of the faculty of turning real or apparent frustration in one direction into success in another. All this is, however, very different from the mere selection of a subject simply because it in all probability will ‘go’ well—that is, will give publishable results even though the work itself consists of nothing more than the repetition of previous investigations with, perhaps, some trifling modification.

Another word of very simple but very practical advice to those who may not yet have commenced, or have but recently commenced research. Begin and keep a log of your scientific ideas—your scientific reading should suggest many such, as well as conversation with fellow workers and observation of unexpected things which nearly always turn up in your own work. By this means you will be gradually accumulating your stock-in-trade. Do not be in a hurry, however, to draw from it at once—let a few years, two or three, be spent in research under the

direction of someone—or, preferably, more than one—of greater experience, and then sit down and take stock. You will be not a little mortified to find that perhaps 90 per cent. of it is worthless, as Faraday says, in your now maturer judgment; but if, indeed, it does not all disappear, you may well rest content.

I have dwelt at some length on the purely scientific aspect of research. I should have liked also to have said something about the problems of industrial research in general and the relations of physical chemistry to modern chemical industry. But I feel at the same time that this has been accomplished in a much more adequate manner in a recent presidential address to the Society of Chemical Industry delivered by my distinguished predecessor, Professor Donnan, under whom I had the privilege of working, and to whose inspiring and stimulating influence, not only his own students, but this University itself owes so much. Let me simply conclude, therefore, by re-emphasising what I have said in regard to the significance of research. Without research a science is impossible. The absence of research and the scientific spirit is, indeed, the negation of science. No one should seriously enter upon any department of science unless he is determined to add his own quota, be it ever so small, to the sum of human knowledge. He owes this to himself, to the Institution which has furnished him with the facilities for the necessary preliminary training, and he owes it to those who have had that training under their immediate control.

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